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The Effect of pH value on Crude Oil and its Fractions Oil-water Interficial Film Dilational Viscoelastic Properties

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Abstract

The study of crude oil and its polar fractions oil-water interfacial film dilational viscoelasticity has important significance to understand the stability of crude oil emulsion. By interfacial expansion rheological determinator, the Gudao Crude oil and its fractions dilational viscoelasticity under different pH value and dilational frequency was tested. The result shows that the dilational modulus of Asphaltene, Resin, Crude oil and Oil fraction reduced gradually under different dilational frequency and pH value, which has a relationship with polar groups in the crude oil and its fractions. When pH value was different, crude oil and its fractions dilational modulus and dilational frequency was similar. Dilational modulus increased with the increases of dilational frequency, but increasing amplitudes were different. Under the same pH value, dilational viscosity and phrase angle of Crude oil and its fractions were decreased with the increase of dilational frequency. The influence degree on different fractions was different, the influence degree of Oil fraction of dilational viscosity and phrase angle was small, Asphaltene was big. The dilational elasticity of Crude oil and its fractions increased with the increase of dilational frequency. Under different dilational frequency, the dilational modulus of Crude oil, Resin and Asphaltene increased with the increase of pH value, and it had no influence on dilational modulus of Oil fraction. The total dilational elasticity tendency of Crude oil, Resin and Asphaltene was increase, while dilational elasticity of Oil fraction decreased with the increases of pH value. The variation of dilational elasticity and phrase angle of Crude oil and its fractions was relatively complex.

keywords: dilational viscoelasticity; pH value; asphaltene; oil-water interfacial film

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1. Introduction

Resin and asphaltene of natural active components in crude oil have a key role in crude oil emulsion. By studying resin and asphaltene interfacial properties in crude oil emulsion stability, previous researchers obtained a lot of significant results [1-7]. During the research of stabilization of water-in-crude oil emulsions from the Norwegian, Johan S etc [1] found that asphaltene has the similar composition with active component extracted from Norwegian crude oil. Besides, there were significant correlations among model emulsion stability prepared by interfacial active component from Norwegian crude oil and real crude oil emulsion stability. Moreover, it was found that crude oil removed interfacial active components was unstable and proved that asphaltene was the main component of natural emulsifier in crude oil. Joseph L. etc [4-7] mainly through determination of asphaltene and its sub fractions monolayer on oil-water interface, got result that certain strength monolayer formed by asphaltene adsorption on oil-water interface will enhance stability of emulsion.

Interfacial dilational viscoelasticity is the key prosperity of fluid interface, which is closely related to the stability of emulsion and foam, and has an important role in agriculture, biological, pharmaceutical and daily chemical industry[8]. Because of interfacial dilational viscoelastic properties depend on the micro-relaxation processes, the parameter of interfacial dilational viscoelasticity will reflect the information of interfacial micro-processes. Sun, T. L etc [9-12] studied aggregation behavior of active fractions in crude oil by interfacial rheology, but the study of crude oil and its four fractions interfacial dilational viscoelasticity was rear.

2. Experimental Section

2.1 Materials

Gudao crude oil from Shengli oil field China. The density of crude oil is 0.9425g.cm^{-3}, the viscosity is 3258 Mpa.s at 50℃. Acetone, n-pentane, Toluene, Sodium Hydroxide (all above is analytical reagent), high-purity Millipore deionized water (resistivity 18MΩ.cm^{-1}).

2.2 Instrument

JMP2000A interfacial dilational viscoelasticity meter, Powereach Ltd., Shanghai,China.

2.3 Experimental method

Dissolved crude oil and its fractions in benzene, and prepared benzene solution with w=0.044% as oil phrase. The different pH value high-purity Millipore deionized water (90 cm^{-3}) was placed in the Langmuir trough, then another 50 cm^{-3} of benzene solution was place on the polymer solution phrase, and was allowed to stand for 3 h to reach the adsorption equilibrium, as detected by steady-state values of dilational modulus under different frequency (0.1000、0.0500、0.0333、0.0200、0.0125、0.0100s^{-1}).

2.4 Experimental principle

Study dilational viscoelasticity of oil-water interfacial film by low amplitude and frequency oscillometry. When the blocks move on the interface with a sine wave, the interface is subjected to periodical expansion and compression. Interfacial tension changes with interfacial area periodically. This deformation leads to a sinusoidal change in surface tension ($d\gamma$), the dilational modulus ε is given by

$$\varepsilon = \frac{d\gamma}{d\ln A} \tag{1}$$

This parameter measures the interface response to a compression or an expansion. For viscoelastic interfaces, the change in surface area and change in surface tension are out of phase, so that the dilational modulus is a complex quantity, with real and imaginary components defined as follows:

$$\varepsilon = \varepsilon_d + i\omega\eta_d \tag{2}$$

The imaginary part of the dilational modulus or loss component is related to the product of the surface dilational viscosity, η_d ($mN \cdot s \cdot m^{-1}$), and the radial frequency $\omega(rad \cdot s^{-1})$.

The absolute value of the complex dilational modulus $|\varepsilon|$ is related to the storage and loss modulus by:

$$\varepsilon_d = |\varepsilon|\cos\theta \tag{3}$$

$$\eta_d = \frac{|\varepsilon|}{\omega}\sin\theta \tag{4}$$

θ is the loss angle of the modulus.

3. Result and Discussion

3.1 The relationship between dilational modulus and dilational frequency of crude oil and its fractions under different pH value

When pH value was 5、7、8、10, the relationship between dilational modulus and dilational frequency of Gudao crude oil, Oil fraction, Resin, Asphaltene oil-water interfacial film can be seen in the following figs 1-4.

By means of figure 1-4, when pH value was 5-10, as the dilational frequency increasing, oil-water interfacial dilational modulus of Crude oil, Resin, Asphaltene was increased. But for the Oil fraction, the total tendency was increased with dilational frequency; interfacial dilational modulus was increased, which shows that the influence of dilational frequency on oil fraction dilational modulus was little. Low levels of pH value indicate that increase amplitude of Resin and Asphaltene dilational modulus with dilational frequency was little small; High levels of pH value indicate that increase amplitude was relatively big. When pH value was low, dilational modulus of crude oil water/oil interfacial film was far less than Resin and Asphaltene. When pH value was high, the difference of oil-water interfacial film dilational modulus of Crude oil, Resin and Asphaltene was smaller. In the adopted frequency and pH value in the experiment, the dilational modulus of Oil fraction, Crude oil, Resin, Asphaltene increased gradually.

Certain structure and strength interfacial film can be formed on oil-water interface by crude oil and its fractions. When interfacial film is subject to periodical compression and expansion, there exist lots of relaxations, such as molecular structure relaxation, dispersion relaxation process of interface and body phrase, interfacial structure relaxation etc. These relaxation processes are manifested as blocking deformation process (viscosity) and restoration process (elasticity).

Oil fraction is mainly composed chain alkane and aromatic hydrocarbon, the interfacial film formed by oil fraction has large compressibility, the interfacial tension changes with film area was relatively small, by means of dilational modulus, the dilational modulus was little small.

Gudao Crude oil, Asphaltene and Resin contain lots of O、S、N elements. These polar substances exist in crude oil and its fractions and contain a lot of active material. The compress ability of oil-water interfacial film was small, the change of interfacial tension with film area was big, and dilational modulus was high. When frequency was low, the deformation ratio of interfacial film under extra force was slow. There was enough time for film forming substance in the oil-water interfacial film to restore the change of interfacial tension produced by interfacial compression and expansion through dispersion and reorientation of molecular. The change of interfacial tension was small, and the dilational modulus of interfacial film was small. In reverse, when frequency was high, the film deformation ratio was fast under extra-force, the restoration time was not enough; the gradient of interfacial tension was big, dilational modulus was big.

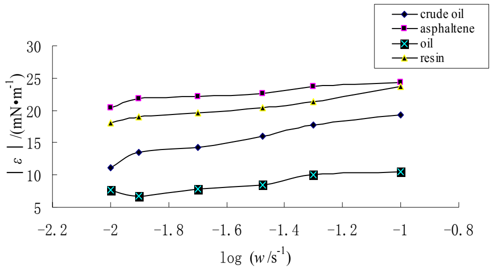

Fig1. pH=5, The relationship between dilatational modulus(ε)and frequency(ω) of oil-water interfacial film for Gudao crude oil and its fractions

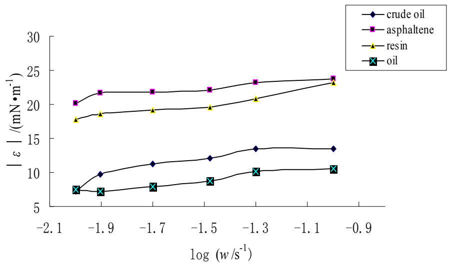

Fig2. pH=7, The relationship between dilatational modulus(ε)and frequency(ω) of oil-water interfacial film for Gudao crude oil and its fractions

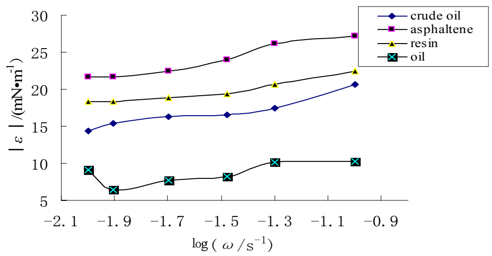

Fig3. pH=8, The relationship between dilatational modulus(ε)and frequency(ω) of oil-water interfacial film for Gudao crude oil and its fractions

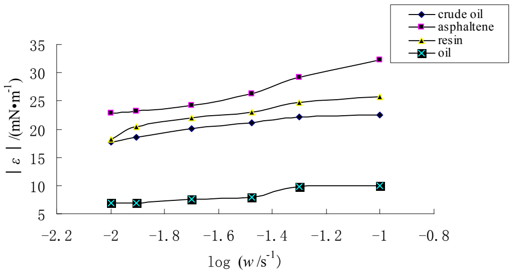

Fig4. pH=10, The relationship between dilatational modulus(ε)and frequency(ω) of oil-water interfacial film for Gudao crude oil and its fractions

3.2 Under different pH value, the relationship between dilational viscosity, dilational elasticity, phrase angle and dilational frequency of crude oil and its fractions

When pH value was 7, the relationship between crude oil and its fractions dilational viscosity, dilational elasticity, phrase angle and dilational frequency were investigated; the result can be seen in fig 5-7.

By means of figure 5, as the dilational frequency increasing, the dilational viscosity of Crude oil, Asphaltene and Resin was decreased, but oil fraction shown as increased at first then decreased. But dilational viscosity of Asphaltene decreased rapidly with dilational frequency and the results showed that the dilational viscosity of Asphaltene was influenced significantly by dilational frequency. The dilational frequency had little influence on dilational viscosity of Crude oil, Resin and Oil fraction. When the dilational frequency was big, the tendency of dilational viscosity was similar. In tested frequency range, the dilational viscosity of Asphaltene was the biggest.

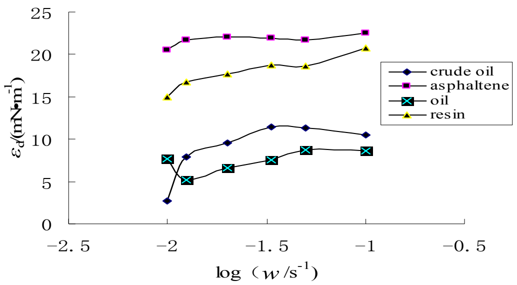

Fig5. The relationship between dilatational elasticity(ε_d) and frequency (ω) of oil-water interfacial film for Gudao crude oil and its fractions

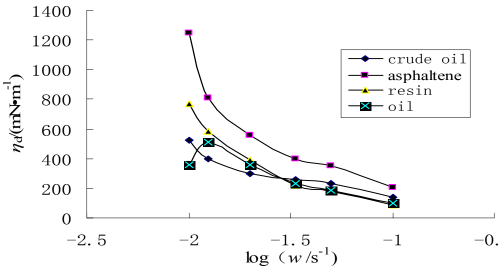

Fig6. The relationship between dilatational viscosity (η_d) and frequency (ω) of oil-water interfacial film for Gudao crude oil and its fractions

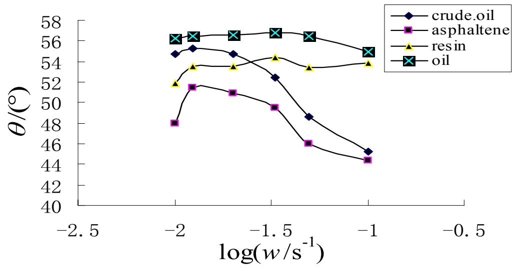

Fig7. The relationship between phase angle(θ)and frequency(ω) of oil-water interfacial film for Gudao crude oil and its fractions

Dilational viscosity reflects the interfacial film blocking deformation ability, its interfacial film fluid properties. It reflects the deformation ratio of interfacial film under extra force. The smaller deformation ratio, the bigger dilational viscosity is.

Under low dilational frequency, dilational viscosity is dominated by the interfacial film structure. The stronger molecular rigid of interfacial film structure is, the greater ability of blocking extra force, the slower interfacial film deformation ratio under unit extra force, the

higher dilational viscosity is. Asphaltene is rich in O、S、N elements and surface active agents, the strength of interfacial film and dilational viscosity of interfacial film are high. As dilational frequency increasing, the interfacial film deformation ratio under extra force increase, interfacial film dilational viscosity decrease gradually.

By means of figure 6, as dilational frequency increasing, dilational elasticity of Asphaltene, resin and resin increased, but increasing extent was not big. The tendency of crude oil and oil fraction dilational elasticity shown as increased at first then decreased. From the results, the dilational elasticity of Asphaltene, Resin, Crude oil and Oil fraction diminished in order under same frequency.

Dilational viscoelasticity reflects the ability of interfacial film restoration, its solid property of interfacial film. The stronger molecular rigid of interfacial film structure is, the greater ability of blocking extra force, the slower interfacial film deformation ratio under unit extra force, the higher dilational viscosity is. Meanwhile, the lower dilational frequency, there were enough time for interfacial film to restore deviation from steady state, the lower dilational elasticity. When dilational frequency was high, there wasn't enough time for interfacial film to restore steady state, deviation from steady state was big, and the dilational elasticity was high. Oil fraction was mainly composed by hydrocarbons molecular, the strength of interfacial film was low, the inter force was low, the dilational elasticity was low. The molecular weight of polar Asphaltene molecules was big; rigid of molecules was strong, the dilational elasticity was high.

By means of figure 7, phrase angle of Oil fraction was the biggest, and phrase angle decreases with the increase of dilational frequency, but decreased degree was small. Phrase angle of Resin with the change of dilational frequency had little change. Phrase angle of Asphaltene and Crude oil decreased rapidly with the increase of dilational frequency. Phrase angle is the phrase difference of the periodical change of interfacial tension and change of extra force on the interfacial film. Every dilational frequency corresponding to a certain phrase angle, the bigger phrase angle was the longer the time of phase difference. Therefore, phase angle reflects the variation speeds of interfacial film with extra force. The compressibility of Oil fraction was good; the extra force on the interfacial film can be buffered through deformation, the reaction of interfacial tension to extra force was slow, phrase angle was big. A great amount of polar groups can be found in Asphaltene, The rigidity of interfacial film was strong, there wasn't buffering processing of interfacial film to the extra force (or every short buffering process), the response of interfacial tension to extra force was fast, phrase angle was small, The interaction reaction of interfacial film to extra force increased with the increase of dilational frequency, phrase angle was reduced [13].

3.3 The effect of pH value on crude oil and its fractions dilational viscoelasticity

Adopt different pH value solution as water phrase, and under frequency of 0.0333HZ, the relationship between pH value and dilational viscoelasticity of Crude oil and its fractions was tested. The results can bee seen in the fig 8-11.

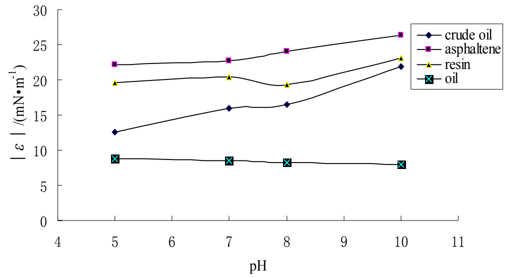

Fig8. The effect of pH value on dilatational modulus(ε)

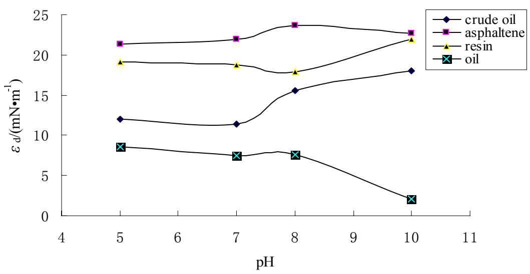

Fig9. The effect of pH value on dilatational elasticity(ε_d)

Figure 8 shows the expansion modulus of crude oil, resin, asphaltene increase with the growing of aqueous phase pH value, which plays little impact on the expansion modulus of oil fractions. This is because mouts of functional group like -COOH, -H and so on react with -OH into anionic surfactant as the pH value increase. The surfactant reduces oil/water surface tension, improves the emulsion stability and enlarge the expansion modulus. It indicates that the pH value have big influence on crude oil emulsion stability.

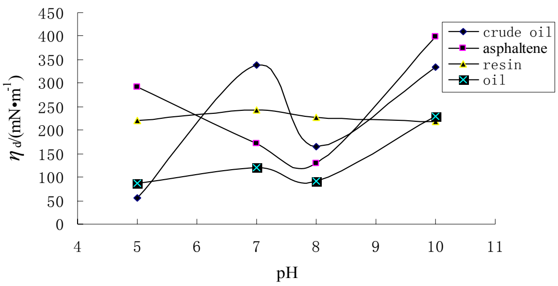

Fig10. The effect of pH value on dilatational viscosity (η_d)

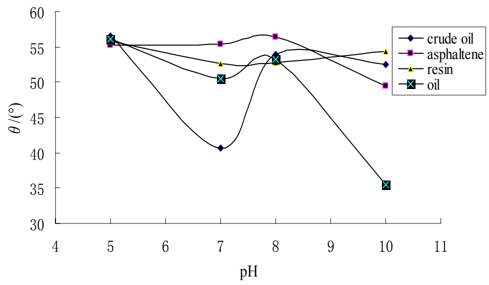

Fig11. The effect of pH value on phase angle(θ)

Figure 9 shows that the trend of expansion elastic in crude oil, resin and asphaltene increase with the growing of aqueous phase pH value, while the oil fractions have a opposite tendency with the above. This is considered that the anionic surfactant build the molecular rigidity in interfacial film structure and the recovery effect are also strengthened by external force. The both lead to higher expansion elastic. On the contrary, oil fractions consist mainly of hydrocarbons. The inferior strength of interfacial film result to lower expansion elastic.

Figure 10 shows that pH value plays different effect on expansion viscosity in different constituent. When the aqueous phase pH value increase, the one of asphaltene decrease at first and then increase. The pH value plays little effect on the viscosity of resin. The complex composition of crude oil makes it hard to find the relation between the viscosity and pH value. The viscosity of oil fractions are smaller for the lack of surface-active obstances.

Figure 11 shows that the phase angle of asphaltene and resin become smaller with the increase of pH value, but the extent change little， which indicates the pH value have little impact on the phase angle. The influence on the phase angle of crude oil are also hard to study. The phase angle of oil fractions become smaller as the pH value increase. When it is in a high pH value, the drop margin get greater and the compressibility of oil fractions become larger.

From the research we can find that the aqueous phase pH value play an important effect on the oil-water interfacial film dilational viscoelastic properties. As the pH value increase, the interface stability of crude oil, asphaltene and resin build up, which keep the emulsion strength. For the influence of pH value to charge in oil, the dilational modulus of asphaltene, resin, crude oil and oil fractions reduce in turn. And H+ , OH- and the heteroatoms like S,N,O in asphaltene, resin, crude react with oil component in crude oil into surfactant, which makes the interfacial tension decrease. At the same time, the change of pH value can affect the ionization degree of asphaltene and resin .This will alter the surface activity and at last influence the stability of the system.

4. Conclusion

The dilational modulus of Asphaltene, Resin, Crude oil and Oil fractions become lower，in addition with the same expansion frequency and pH value, which has relation with the amount of polar group in crude oil and its fractions. S、N、O exist in Asphaltene、Resin and crude oils，so they have higher interfacial activity。

At different pH values，crude oil has a similar relation curve of Dilational modulus and expansion frequency with its fractions. As the expansion frequency become larger, the dilational modulus becomes bigger. But the margin is not the same. Because of the structure in Asphaltene and resin, they have a higher number.

With the same pH value, the expansion viscosity and phase angle of crude oil and its fractions become smaller as the increase of expansion frequency. But we can find different influence in the crude oil and its fractions. The oil fractions have a small impact. The Asphaltene have a big impact. The expansion elastic of crude oil and its fractions increase with the growing of expansion frequency.

Dilational modulus of crude Oil, Resin and Asphaltene become greater with the increase of pH value, when the dilational frequency was same. But the oil fractions play no effect on the dilational modulus. The tendency of dilational modulus in crude Oil, Resin and Asphaltene is increasing, while the fractions are just the opposite. The change law of expansion elastic and phase angle in crude oil and its fractions looks complex, because the active component of crude oil and its fractions vary in different pH value. Then the forming interfacial film has different stability.

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